

**BIOSPHERIC-ATMOSPHERIC COUPLING ON THE EARLY EARTH**

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Over the history of our planet, the production of gases within the biosphere and their release into the atmosphere have had a very significant impact on the composition and chemistry of the global atmosphere. Important atmospheric gases produced in the biosphere include oxygen ( $O_2$ ), nitrous oxide ( $N_2O$ ), nitric oxide ( $NO$ ), methane ( $CH_4$ ), and ammonia ( $NH_3$ ). Photochemical calculations have been performed to assess the relationship between the magnitude of the biospheric source of these gases and their atmospheric abundance in the oxygen-free and later oxygen-evolving atmosphere. The evolution of oxygen in the atmosphere impacted the composition and chemistry of the atmosphere in several different ways: (1) Oxygen controlled the origin and evolution of atmospheric ozone ( $O_3$ ), (2) Oxygen and ozone control the rates of molecular photolysis in the ultraviolet, and, hence, control many photochemical processes in the atmosphere, (3) Oxygen controls the oxidation state of the biosphere and, hence, controls the chemical nature of the production of gases, i. e., oxidizing vs. reducing gases, and (4) The origin of atmospheric oxygen led to the possibility of lightning-inducing fires, a significant source of many atmospheric gases, including carbon dioxide, carbon monoxide, methane, nonmethane hydrocarbons, and nitric oxide.

Theoretical calculations performed with a one-dimensional photochemical model have been performed to assess the biospheric-atmospheric transfer of gases. Ozone reached levels to shield the Earth from biologically lethal solar ultraviolet radiation (220-300 nm) when atmospheric oxygen reached about 1/10 of its present atmospheric level. In the present atmosphere, about 90 percent of atmospheric nitrous oxide is destroyed via solar photolysis in the stratosphere with about 10 percent destroyed via reaction with excited oxygen atoms. The reaction between nitrous oxide and excited oxygen atoms leads to the production of nitric oxide in the stratosphere, which is responsible for about 70 percent of the global destruction of oxygen in the stratosphere. In the oxygen-/ozone-deficient atmosphere, solar photolysis destroyed about 100 percent of atmospheric nitrous oxide, relegating the production of nitric oxide via reaction with excited oxygen to zero. Our laboratory and field measurements indicate that atmospheric oxygen promotes the biogenic production of  $N_2O$  and  $NO$  via denitrification and the biogenic production of methane by methanogenesis.